

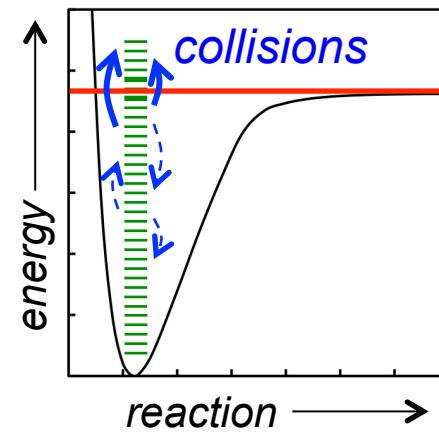
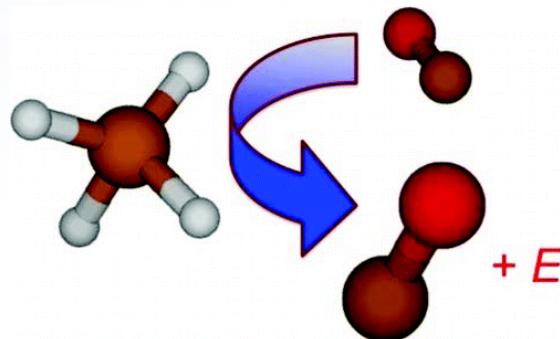


“Third-body” collision efficiencies for combustion modeling: Hydrocarbons in atomic and diatomic baths

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Principal goal: Enable more detailed descriptions of pressure-dependence in chemical kinetic mechanisms



Reaction	Kinetic parameters		
OH+H ₂ =H ₂ O+H	2.144E8	1.52	3449.
O+OH=O ₂ +H	2.57E13	-0.1589	-479.68
O+H ₂ =OH+H	0.506E+05	2.670	6290.000
H+O ₂ (+M)=HO ₂ (+M)	5.8E11	0.6724	-290
	LOW / 7.2E20	-1.73	536 /
	TROE / 0.72	1E-30	1E30 1E30 /
	AR/0.5/	H ₂ O/10/	CO ₂ /2/ CH ₄ /3/
OH+HO ₂ =H ₂ O+O ₂	1.9E16	-1.0	0.0
H+HO ₂ =2OH	1.69E14	0.0	874.
H+HO ₂ =H ₂ +O ₂	4.28E13	0.0	1411.
H+HO ₂ =O+H ₂ O	3.01E13	0.0	1721.
O+HO ₂ =O ₂ +OH	3.25E13	0.0	0.0
2OH=O+H ₂ O	4.331E3	2.7	-2485.7
CH ₃ +OH=CH ₃ OH	4.498E8	1.3	-54590
...			
C3H ₈ +C2H ₅ =C3H ₇ (i)+C2H ₆	1.51E+00	3.46	7470.0
C3H ₈ +C2H ₅ =C3H ₇ (n)+C2H ₆	9.03E-01	3.65	9140.0
C3H ₈ +CH ₂ CHCH ₂ =C3H ₆ +C3H ₇ (n)	2.35E+02	3.3	19842.0
C3H ₈ +CH ₂ CHCH ₂ =C3H ₆ +C3H ₇ (i)	7.83E+01	3.3	18169.0
C3H ₇ (n)(+M)=C2H ₄ +CH ₃ (+M)	1.23E+13	-0.1	30202.0
...			

For example,

$$\text{CH}_3+\text{H}(+\text{M})=\text{CH}_4(+\text{M}) \quad \begin{matrix} 6.925\text{e}13 & 0.18 & 0. \\ 3.8\text{E}39 & -6.564 & 6744. \end{matrix} \quad \begin{matrix} k_{\infty} \\ k_{0,\text{Ar}} \\ F \\ m_M \end{matrix}$$
$$\text{LOW /} \quad \begin{matrix} 0.7 & 10063. & 456.1/ \\ \text{H}_2/2.86/ & \text{H}_2\text{O}/8.57/ & \text{CH}_4/2.86/ & \text{N}_2/1.43/ \end{matrix}$$

$$k(T) = \frac{k_{\infty} k_{0,M}[\text{M}]}{k_{\infty} + k_{0,M}[\text{M}]} F$$

$$k_{0,M} = m_M k_{0,\text{Ar}}$$

Here we calculate m_M ($M = \text{He}, \text{Ne}, \text{Ar}, \text{Kr}, \text{H}_2, \text{N}_2, \text{O}_2$) relevant to the unimolecular kinetics of 38 hydrocarbons (linear, cyclic, branched alkanes, alkenes, radicals)

The physical origin of pressure dependence in kinetics

$$\mathcal{M}_M = k_{0,M} / k_{0,\text{Ar}}$$

In the high pressure limit (k_∞)

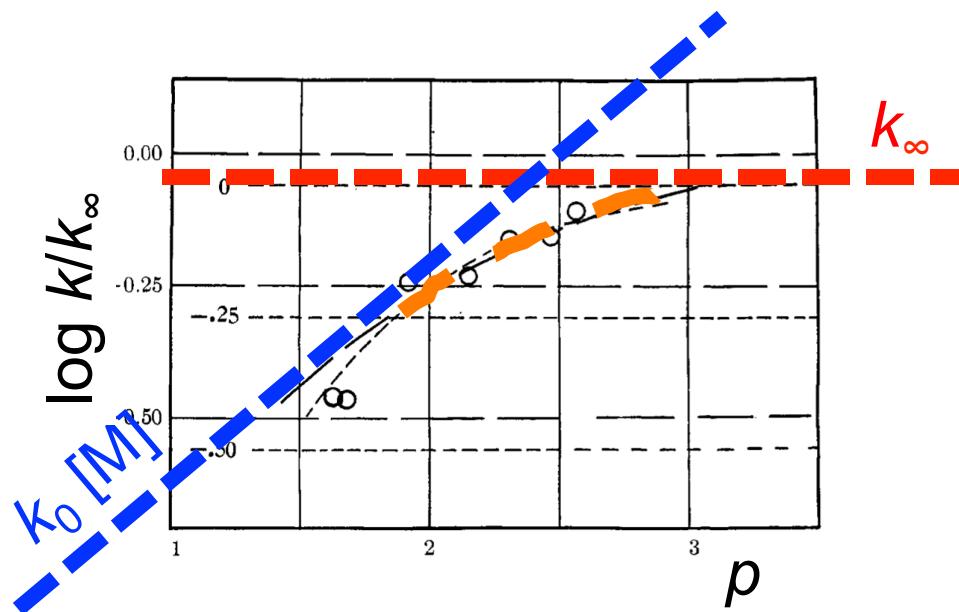
$$k_{\text{TST}} \ll k_{\text{activating collisions}}$$

The TS is rate limiting

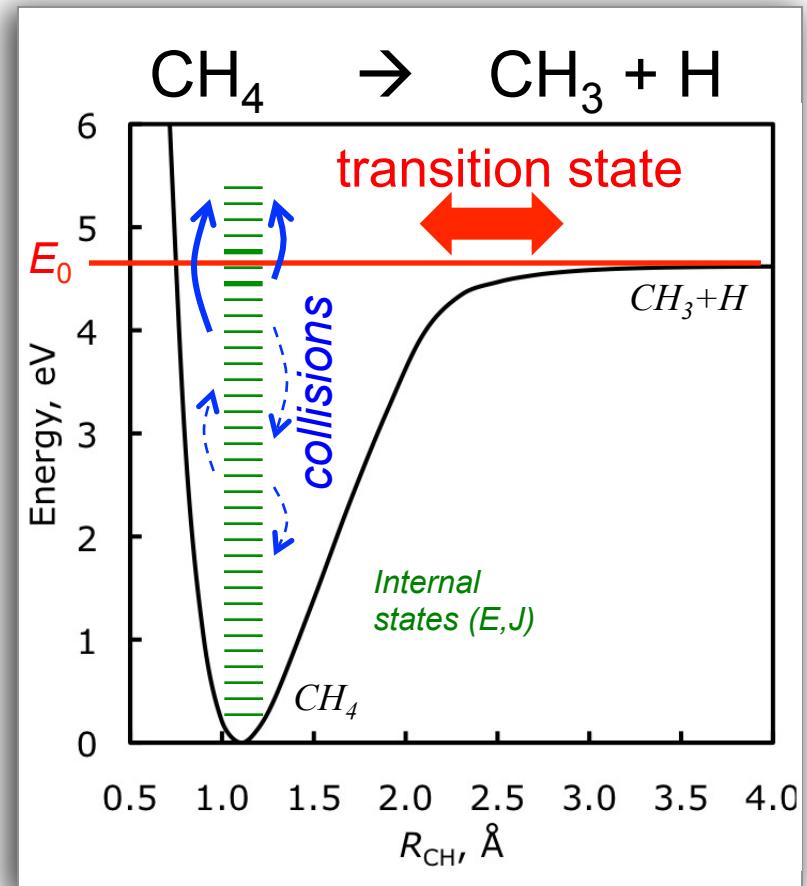
In the low pressure limit ($k \propto k_0 p$)

$$k_{\text{TST}} >> k_{\text{activating collisions}}$$

Activating collisions are rate limiting



O. K. Rice & H. C. Ramsperger, JACS, 1927



Competition modeled via
the master equation

$$\text{Theory: } \mathcal{M}_M = k_{0,M} / k_{0,\text{Ar}}$$

Information required for predicting k_0 for $\text{C}_x\text{H}_y + \text{M}$

$Z(T)$ = collision rate

$P(E,J \leftarrow E',J')$ = state-to-state collisional transfer probability

In many elementary kinetics applications...

Lennard-Jones collision rates Z from tabulated σ and ε

“Single exponential down” model

$P(E \leftarrow E') \approx C \exp(-\Delta E/\alpha)$

$\alpha \approx \langle \Delta E_{\text{down}} \rangle$, average ΔE in deactivating collisions

$\alpha = \alpha_{300} (T/300 \text{ K})^n$, empirical parameters

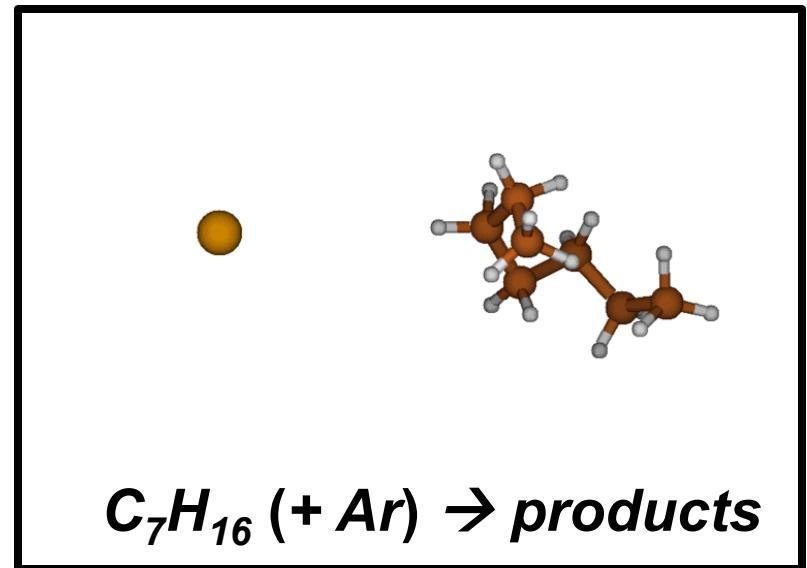
Recent improvements...

Calculated collision rates Z

Detailed models for $P(E,J \leftarrow E',J')$ w/ the 2D master equation

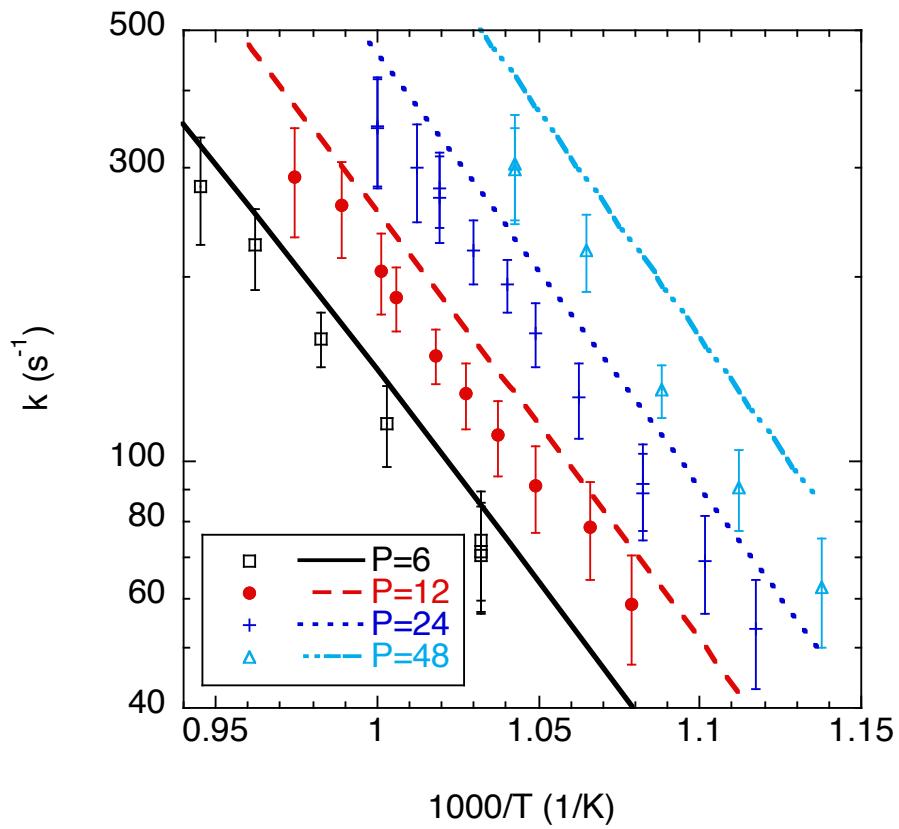
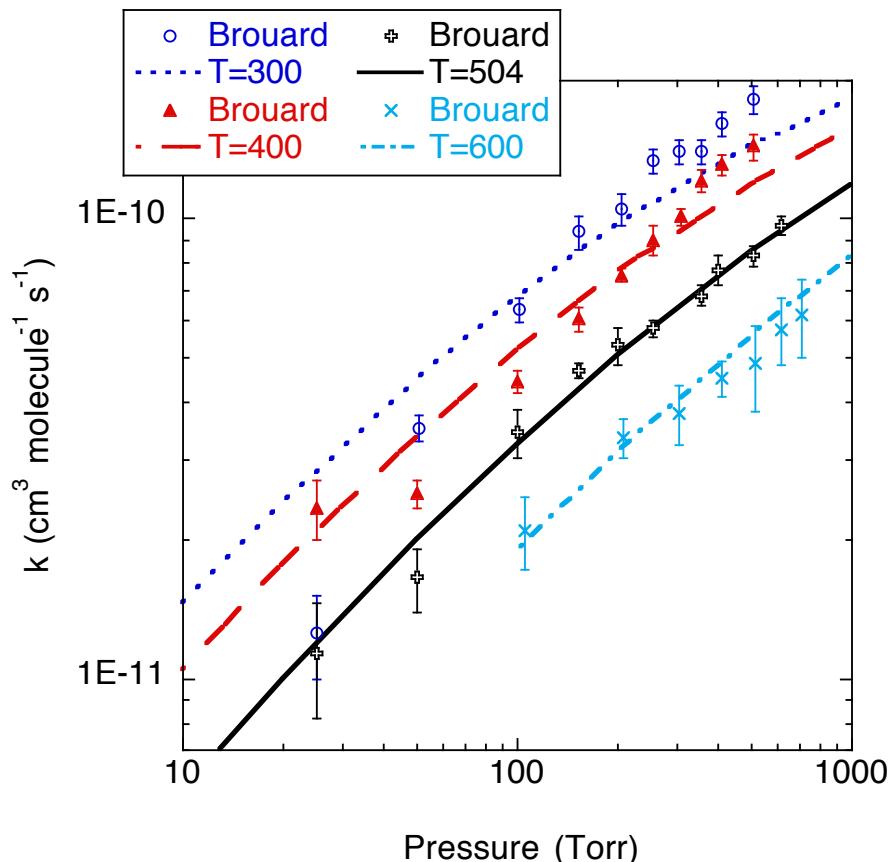
Consideration of several low-order trajectory-based moments of ΔE and ΔJ

e.g., $\langle \Delta E_{\text{down}} \rangle$, $\langle \Delta E_{\text{up}} \rangle$, $\langle \Delta J_{\text{down}} \rangle$, ..., $\langle \Delta E_{\text{down}} \Delta J_{\text{down}} \rangle$, ...



First-principles pressure dependent kinetics w/ Kenley Pelzer, Miller, Harding & Klippenstein

Argonne



~20% errors relative to experiment

exps: Brouard, Macpherson, Pilling,
JPC 93, 4047 (1989) & Knyazev, Slagle,
JPC 100, 16899 (1996)

Approximate methods are useful for \mathcal{M}_M

$$\mathcal{M}_M = k_{0,M} / k_{0,\text{Ar}}$$

$$\begin{aligned}\mathcal{M}_M &= k_{\text{SC},M} \beta_{c,M} / k_{\text{SC},\text{Ar}} \beta_{c,\text{Ar}} \\ &= Z_M \beta_{c,M} / Z_{\text{Ar}} \beta_{c,\text{Ar}}\end{aligned}$$

Troe's weak collider approximation
JCP 66, 4745 (1977)

$$\beta_c = \left(\frac{\alpha}{\alpha + F_E k_B T} \right)^2$$

Z = collision rate

α = $\langle \Delta E_{\text{down}} \rangle$

F_E : proportional to the relative thermal state population of the unimolecular reactant above threshold

at low T , $\alpha \approx F_E k_B T$

$$\mathcal{M}_M \approx Z_M \alpha_M / Z_{\text{Ar}} \alpha_{\text{Ar}}$$

at high T , $\alpha \ll F_E k_B T$

$$\mathcal{M}_M \approx Z_M \alpha_M^2 / Z_{\text{Ar}} \alpha_{\text{Ar}}^2$$

Approximate methods are useful for \mathcal{M}_M

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$Z = \text{collision rate}$
 $\alpha = \langle \Delta E_{\text{down}} \rangle$

Good PESs &
classical trajectories

F_E : proportional to the relative thermal
state population of the unimolecular
reactant above threshold

at low T , $\alpha \approx F_E k_B T$

$$\mathcal{M}_M \approx Z_M \alpha_M / Z_{\text{Ar}} \alpha_{\text{Ar}}$$

at high T , $\alpha \ll F_E k_B T$

$$\mathcal{M}_M \approx Z_M \alpha_M^2 / Z_{\text{Ar}} \alpha_{\text{Ar}}^2$$



Good (& cheap) “universal” PES for $C_xH_y + M$

$M = He, Ne, Ar, Kr, H_2, N_2, O_2$

Universal $C_xH_y + M$ PES:

“TB+exp/6”

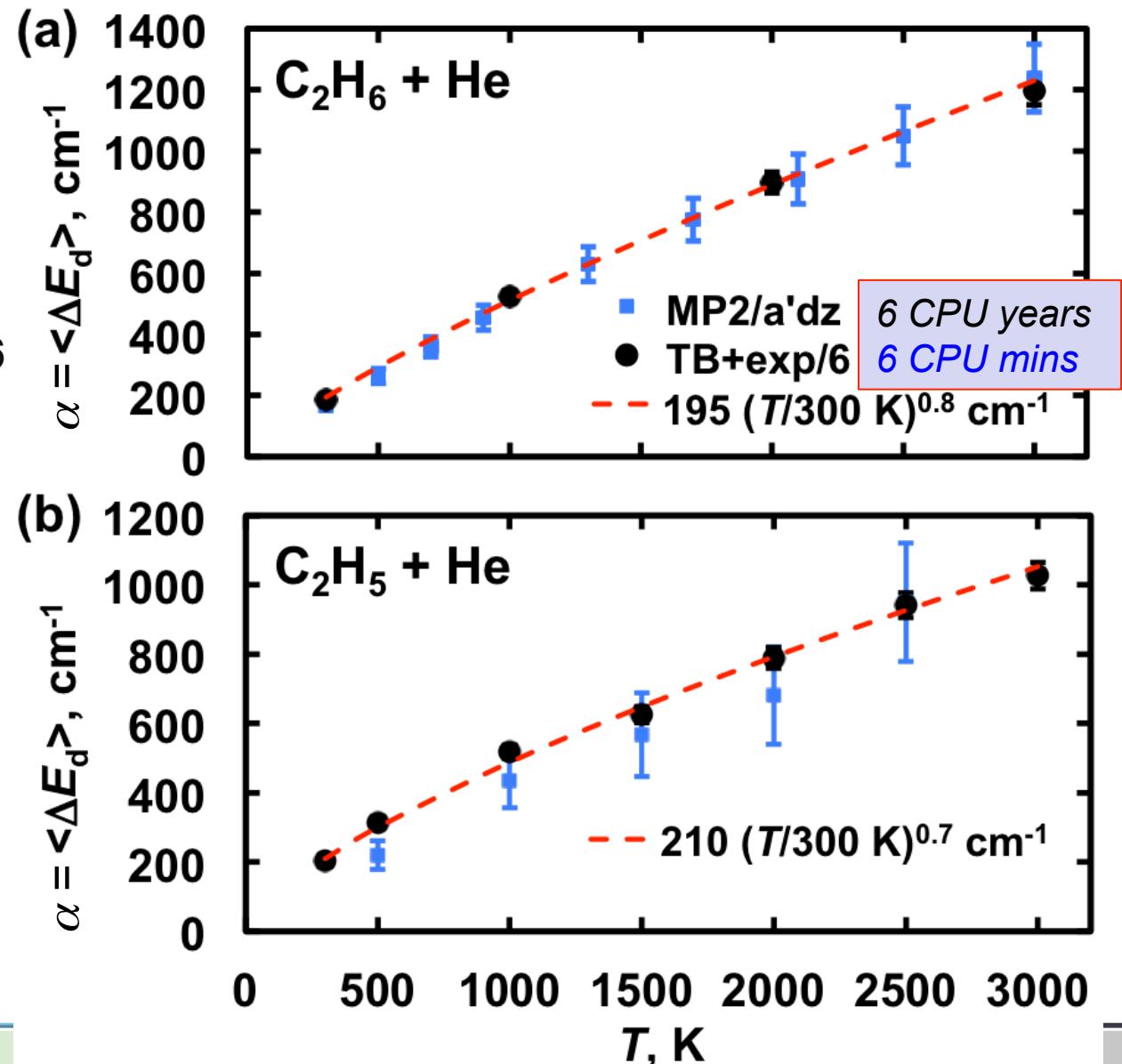
C_xH_y : Extended Hückel theory
(tight binding)

+M: pairwise atom-atom exp/6
terms fit for $\underline{CH_4} + M$

Validation target:

“direct” trajectories

MP2/aug'-cc-pVDZ validated
against CCSD(T)/CBS
energies



Calculated collision rates Z for $C_xH_y + M$

Calculate **effective** binary 12/6 LJ parameters from the full-dimensional PESs via averaging over $C_xH_y + M$ relative orientations

Avoids empiricism (e.g., LJ combining rules)

Provides a consistent set of Z to aid in identifying trends

Efficiently treat the 266 systems considered here

Bad: Orientation-average then minimize (~40% errors in Z)

Good: Minimize then orientation-average (<10% errors in Z)

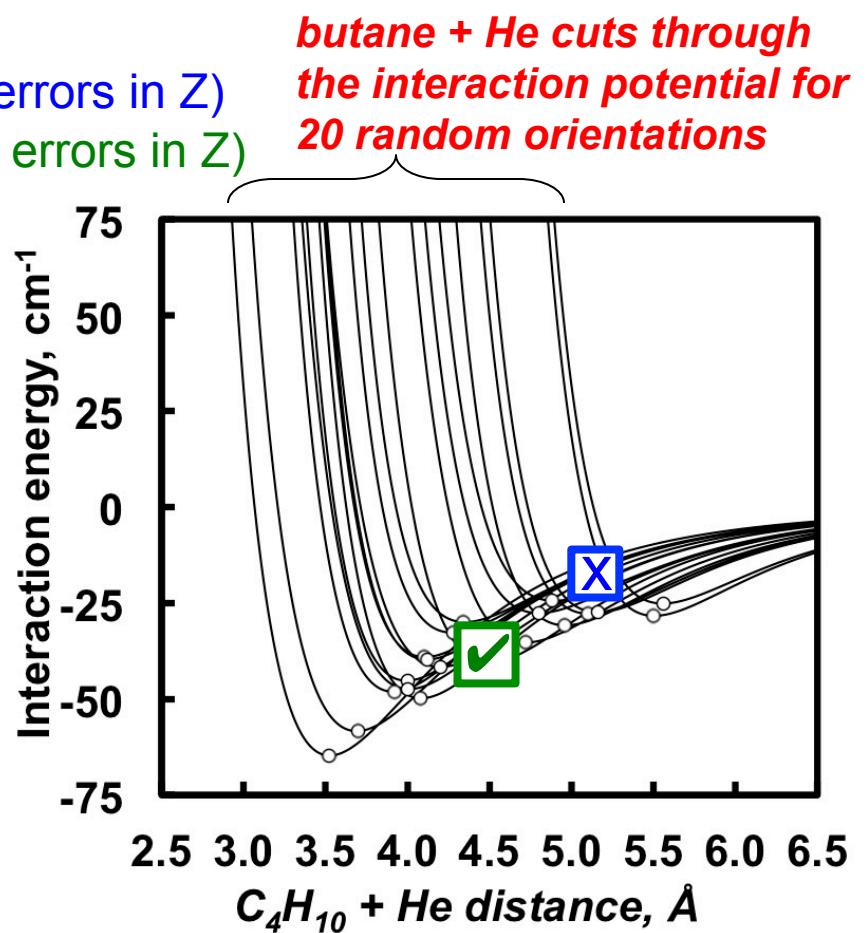
w/ Jim Miller, C&F 161, 101 (2014)

Simple trends for $C_xH_y + M$ relative to $CH_4 + M$

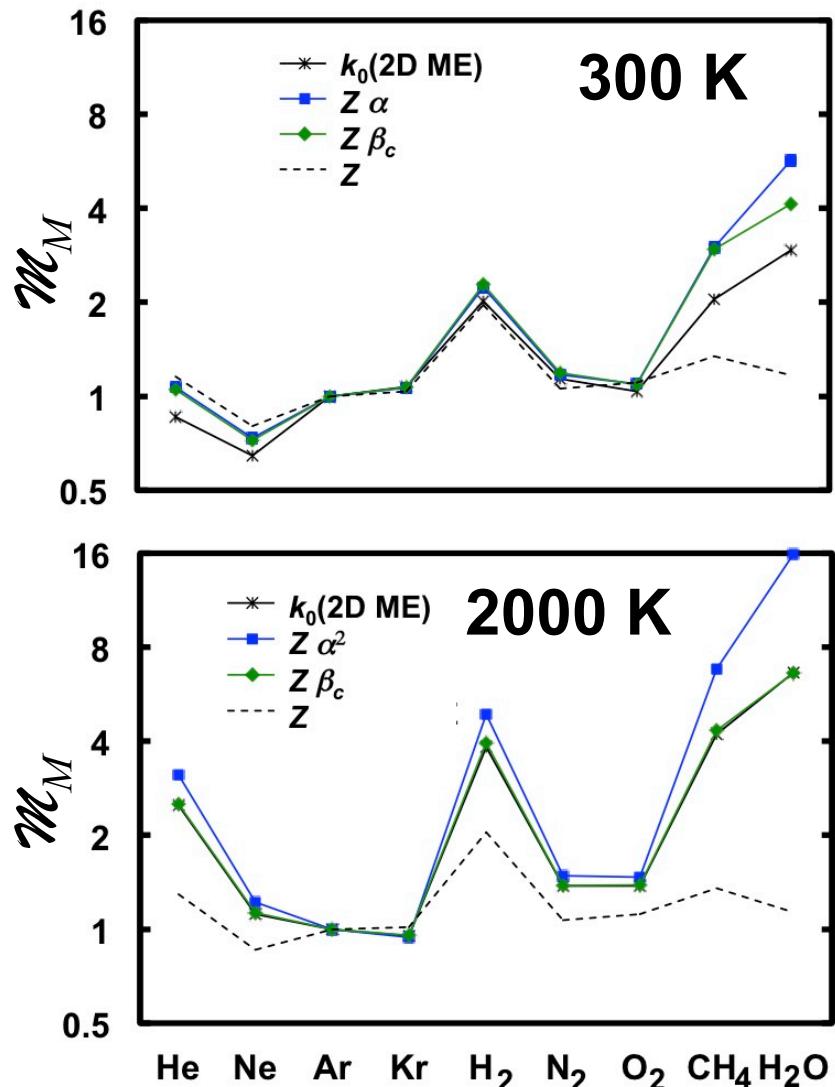
$$\sigma = \sigma_{CH_4+M} x^{0.15}$$

$$\varepsilon = \varepsilon_{CH_4+M} x^{0.25-0.40}$$

predicts 266 calculated binary 12/6 LJ collision rates to better than 5%



Relative bath gas efficiencies for $\text{CH}_4 + \text{M}$



9 baths

4 atomic baths

3 diatomic baths

2 polyatomic baths for $\text{CH}_4 + \text{M}$

w/ Miller, Klippenstein, JPCA 117, 12243 (2013)

3 methods

2D ME : A detailed ME calculation

$Z \beta_c$: Troe's method

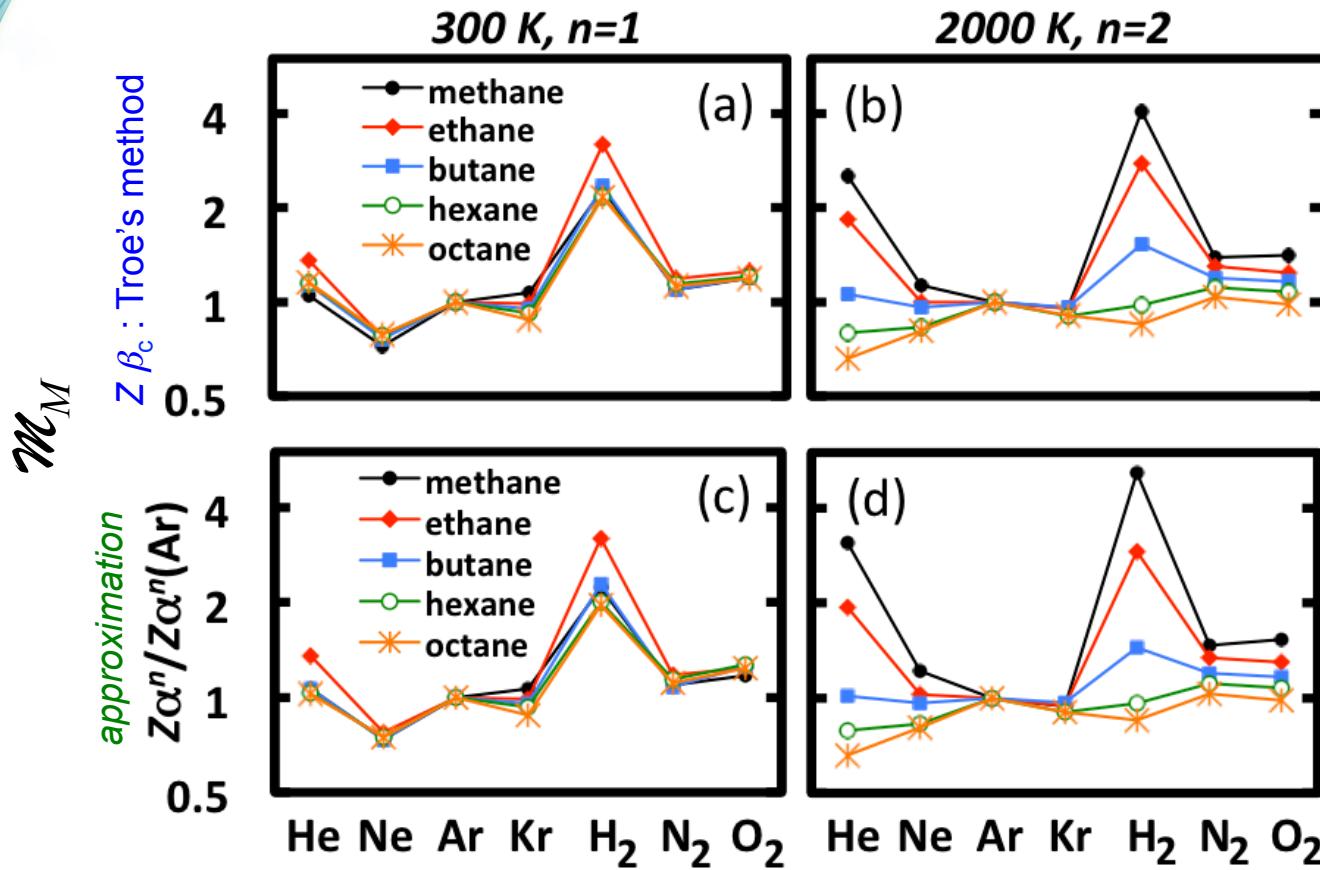
$Z \alpha^n$: Approximation to Troe's method
 α calculated via classical trajectories

Conclusions

- The simpler methods agree with the 2D ME for the atomic and diatomic baths; more detailed methods may be required for the polyatomic baths
- Relative efficiencies are T -dependent
- $\text{H}_2\text{O} > \text{CH}_4 = \text{H}_2 > \text{He} > \text{Ar} = \text{Kr} = \text{N}_2 = \text{O}_2$
- $m_{\text{H}_2\text{O}} = 3$ at 300 K and 7 at 2000 K

Trends in bath gas efficiencies

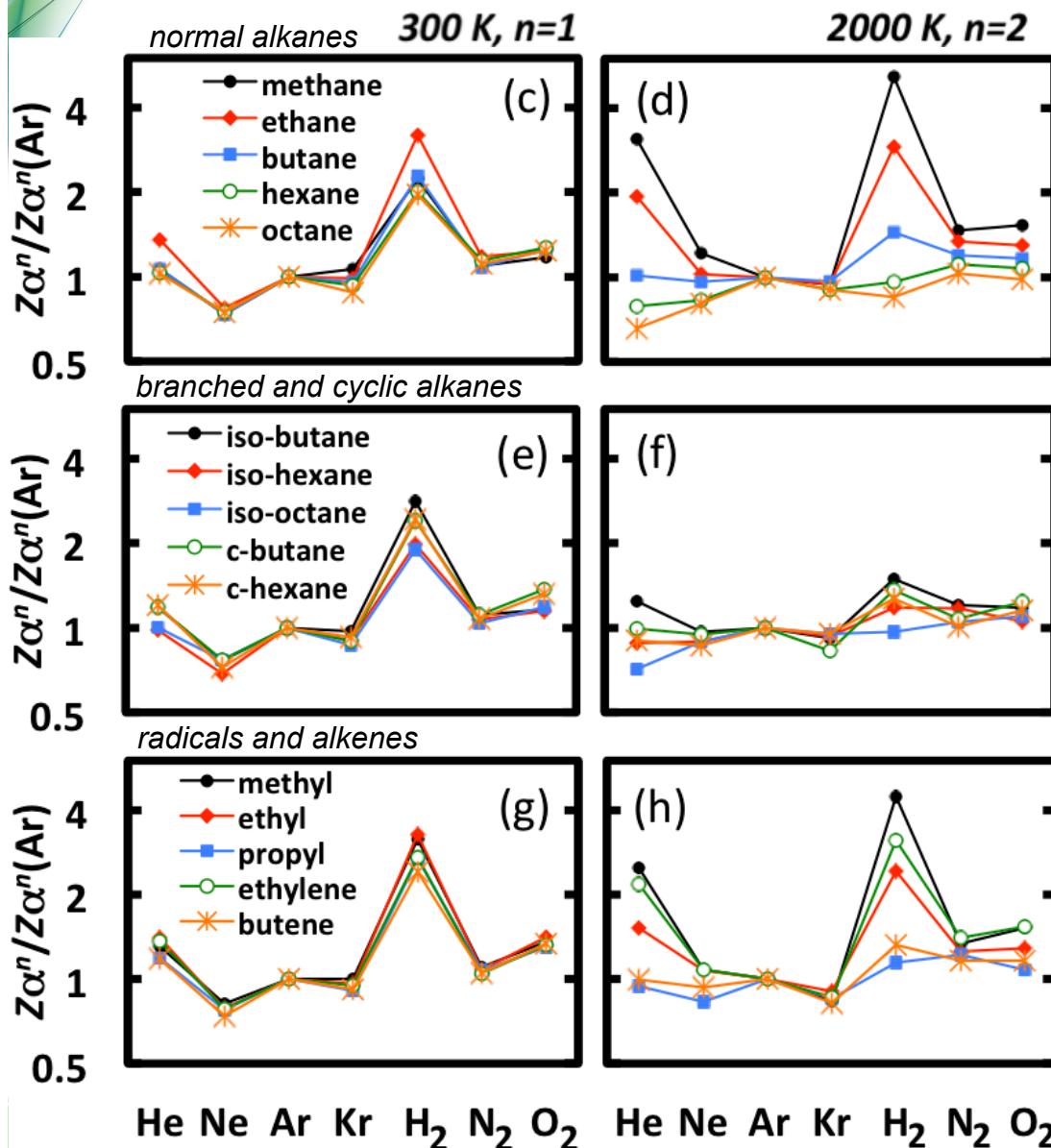
5 *n*-alkanes in 7 baths



The approximation to
Troe's expression is
accurate for m_M

Trends in bath gas efficiencies

15 species in 7 baths



T-dependence in m_M

- m_M is insensitive to size, structure of unimolecular reactant at 300 K
- More sensitivity at 2000 K

Size-dependence in m_M

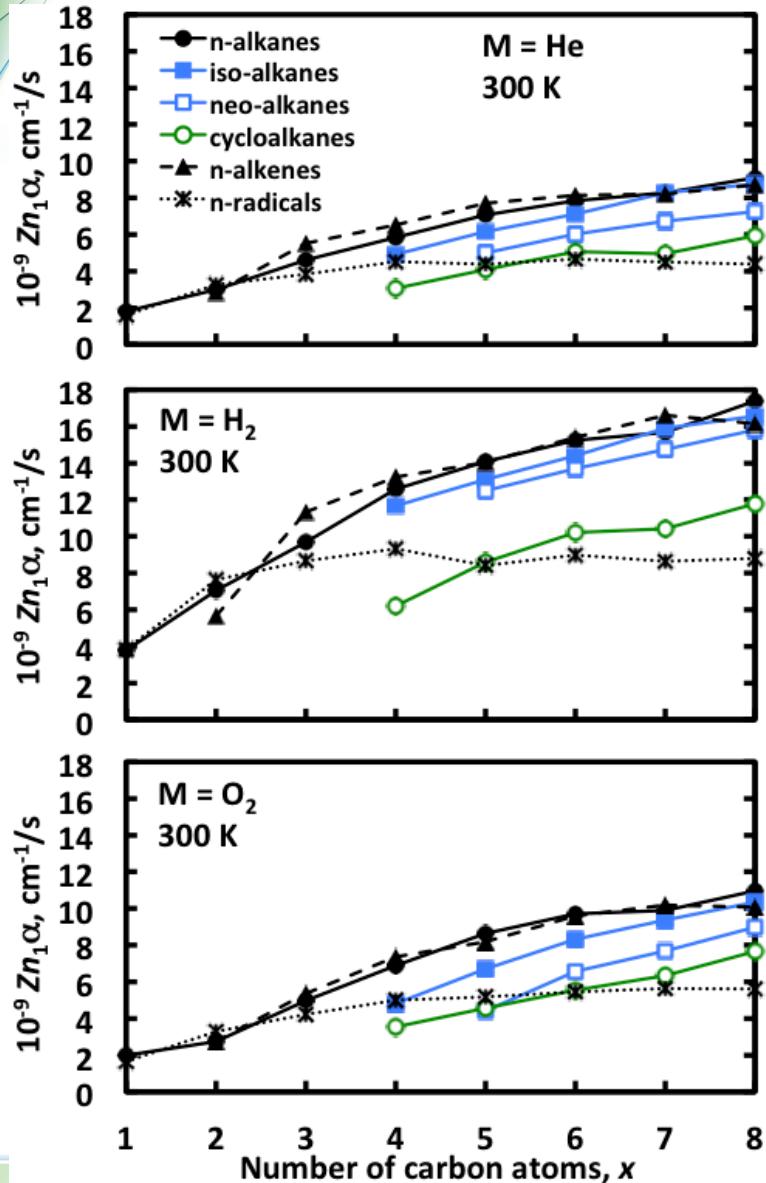
- Significant in m_{He} & m_{H_2} for systems smaller than C₃

Structure-dependence in m_M

- Less M-dependence for branched & cyclic species than for linear species

Trends in bath gas efficiencies

38 species C_xH_y in 3 baths



Linear species

- Alkanes are similar to alkenes
- Alkyl radicals are similar at low x , “converge” around $x = 3$ due to lower D_0

Branched species

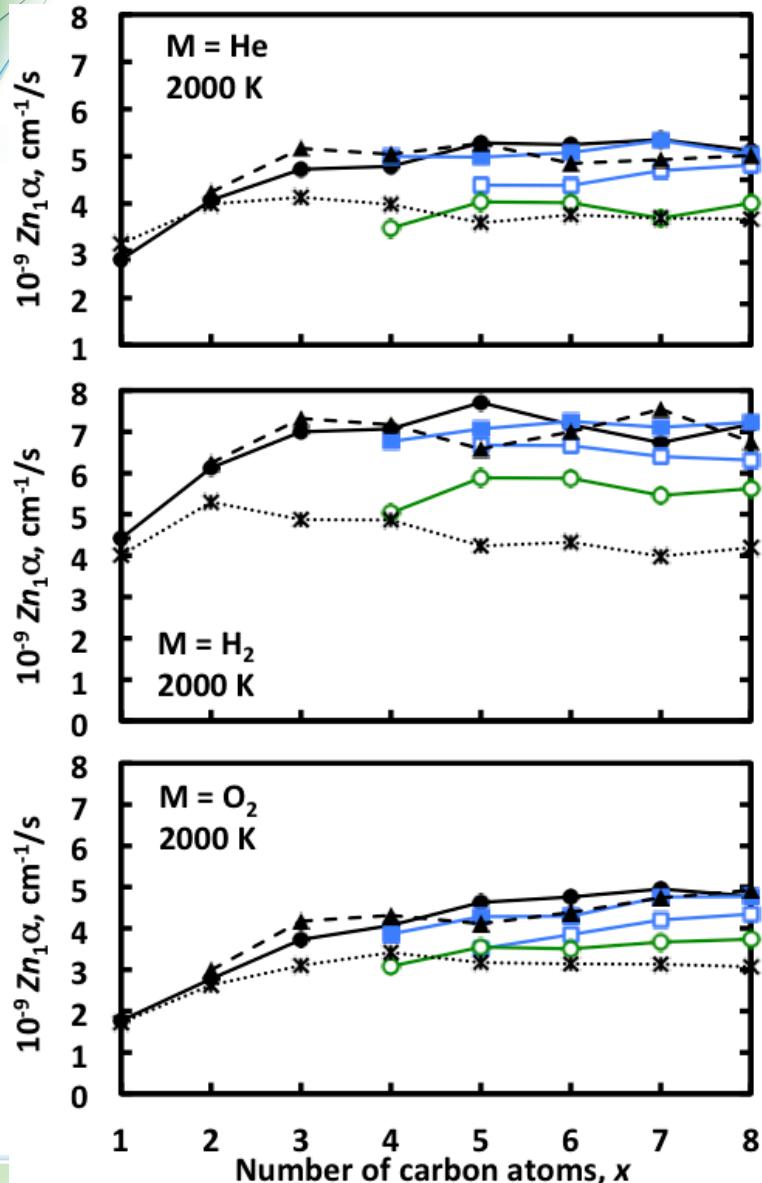
- Number of in backbone is most important
- iso-C_xH_y = normal-C_{x-1}H_y
- neo-C_xH_y = normal-C_{x-2}H_y

Cyclic species

- No straightforward “shift” relative to others
- Lower efficiencies due in part to lower D_0

Trends in bath gas efficiencies

38 species C_xH_y in 3 baths



At higher T

- Similar trends
- Earlier “convergence” with respect to x; likely controlled by D_0/α



Summary

New $C_xH_y + M$ potentials & classical mechanics enable:

- Accurate calculations of Z and α
- Useful practical calculations of \mathcal{M}_M for building large detailed kinetic models
- Rationalizations of trends in \mathcal{M}_M with respect to
 - Bath gas identity (mass, internal structure, etc.)
 - Bath temperature
 - The size of the unimolecular reactant
 - The chemical structure of the unimolecular reactant

Codes and potentials freely available online sandia.gov/~ajasper

Future work: Calculate \mathcal{M}_M for oxygenated species, PAHs, etc...

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